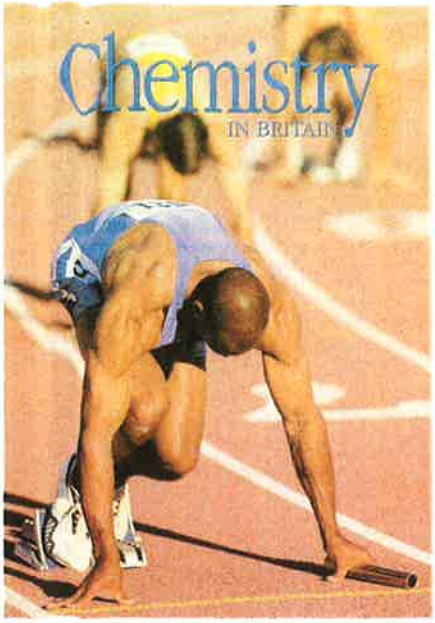

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A PET subject

Plastic bottles now come in all shapes and sizes, and Dave Birkett is betting that the market for PET will continue to grow

ABOUT 20 YEARS AGO I PLAYED A (minor) part in a project aimed at developing barrier coatings for polyethylene terephthalate (PET) drink bottles. The project was successful, and the by now well-known 2 l beer bottle started to appear in off-licences in the UK. The expectation in the British packaging industry in the 1980s was that it was only a matter of time before the half-pint glass bottle went the way of the party can and that the idea would soon spread around the world.

My career then took me away from both coatings and the UK, so that I failed to notice that such expectations were only correct if 'only a matter of time' and 'soon' were viewed in the timescale of decades rather than years. For it was not until 1999 that the US brewer Miller first introduced the 16 fluid ounce (0.45 l) polyester beer bottle into the US. So how was it that the first step was so successful, yet the next steps took so long?

The first part of the question is answered by considering the properties of PET, which was originally developed for fibres. *Box 1* describes the early history and manufacture of the polymer. In the late 1950s researchers found that the molten polymer could be extruded through a slot to give a highly transparent film for flexible packaging. Because the polymer

1. History in the making

Polyesters, that is the reaction products of polyhydric alcohols and polybasic organic acids, have been known academically, and even used commercially since well before Staudinger and Carothers' elucidation of polymer structures in the 1920s and 1930s. The first commercial synthetic polyesters were glyceryl phthalate (glyptal) resins used in coatings as early as World War I, followed shortly afterwards by alkyd resins (glyptals modified with unsaturated long chain monocarboxylic acids derived from natural oils) also used in paints.

But DuPont's launch of Nylon (a linear polyamide) in the late 1930s gave rise to a search for other fibre-forming polymers. Linear polyesters were an obvious choice, but if they were made from aliphatic dicarboxylic acids their hydrolytic stability was too low. Polyesters of the aromatic phthalic acid (benzene-1,2-dicarboxylic acid) were better in this respect, but the conformation forced on the polymer molecules by the *ortho*-orientation of the two carboxylic groups meant that such polymers weren't really suitable for stretching into fibres. However, this is not a problem with the *para*-isomer, terephthalic acid (benzene-1,4-dicarboxylic acid). The simplest polyester of this, that with ethylene glycol (ethane-1,2-diol), proved to be an excellent fibre-forming polymer, and was first launched by ICI shortly after World War II as Terylene. Polyethylene terephthalate now represents over 50 per cent of world synthetic fibre manufacture.

The polymer is prepared in a two stage process. Initially ethylene glycol and terephthalic acid (or its dimethyl ester) are reacted to give bis-(2-hydroxyethyl)-terephthalate (BHET). This is further reacted with an antimony catalyst to give a high molecular weight polymer (n = 130–150/where n = number of monomer units). The reaction conditions are chosen to maximise the yield of polymer while minimising side reactions, such as decomposition of end-groups to give acetaldehyde (ethanal).

The world capacity for PET resin (for all applications) is in the region of 9.5m t per annum. The largest producer is Voridian (a division of Eastman Chemical Company in the US) with approximately 1.4m t pa capacity, followed by Wellman, KoSa (a US–Mexican joint venture) and Mossi & Ghisolfi (Italy). □

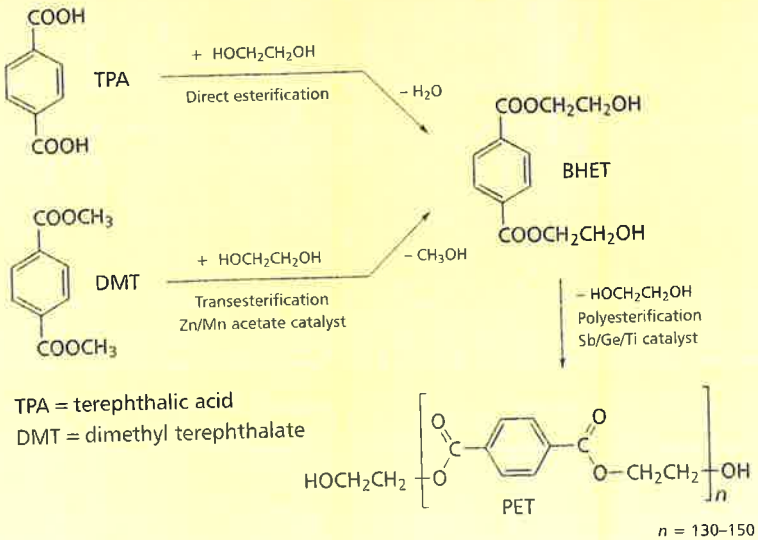
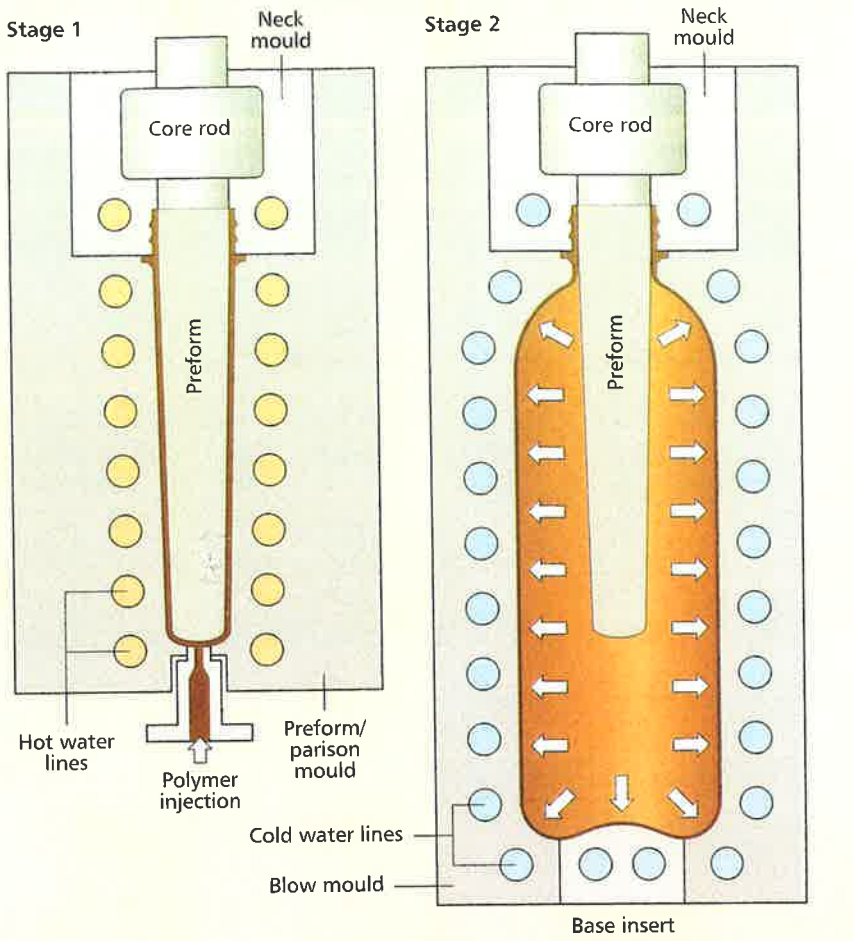


Fig 1. The blow moulding process; in stage 1 the preform is injection moulded, in stage 2 the preform is inflated to the shape of the blow mould



2. Barrier polymers

The rate at which a gas can permeate through a polymer depends on the solubility of the gas in the polymer, and the mobility of the gas molecules once they get there. Both of these depend in turn on the polarity of the gas and the polymer, the density and crystallinity of the polymer, the temperature and the humidity. Prediction is thus difficult, but what we know empirically for oxygen and carbon dioxide is that polymers with a large number of polar groups such as —OH, —CN, —Cl show the lowest transmissions. If they can be kept dry, regenerated cellulose (Cellophane) and polyvinyl alcohol, $-(CH_2CHOH)_n-$, prepared by hydrolysing polyvinyl acetate, show excellent barrier properties. Indeed Cellophane was for a long time the material of choice for crisp bags. However, as the humidity rises the permeability of both these polymers increases rapidly (polyvinyl alcohol is in fact water soluble). Nor are either suitable for coextrusion in multilayer packaging films.

But if instead of hydrolysing a vinyl acetate homopolymer we start with a copolymer of vinyl acetate and ethylene then we eventually obtain EVOH – an ethylene vinyl alcohol resin. This retains much of the barrier performance of Cellophane or polyvinyl alcohol, but is much easier to process. It is still moisture sensitive, although less so than polyvinyl alcohol, and therefore tends to be found sandwiched between two layers of a cheaper and more hydrophobic resin such as PET.

Resins based on acrylonitrile ($CH_2{=}CHCN$) also find uses as the barrier layers in food packaging, but much better known is PVDC (polyvinylidene chloride): $(CH_2CCl_2)_n$—. As a copolymer with small amounts of other monomer this is familiar as Saran Wrap (a trademark of Dow) and some clingfilms (although most clingfilms are made from PVC or polyethylene).

PVDC is less easy to recycle than EVOH. The problem is that prolonged heating, especially in the presence of base, can lead to the discolouration and even decomposition of the polymer via dehydrochlorination:

$$-(CH_2CCl_2)_n- \longrightarrow -(CH{=}CCl)_n- + HCl$$

$$-(CH{=}CCl)_n- \longrightarrow C + HCl$$

can have a high degree of crystallinity, the films are strong and creep resistant, compared with polyethylene for instance. By the 1970s, blow moulded bottles (*Fig 1*) made from high purity food grades of the resin were beginning to appear and were used for carbonated soft drinks and mineral waters. This is now a huge business: for example the US produced somewhere in the region of 40 000m PET beverage bottles in 2001.

Such simple bottles, however, weren't suitable for beer. Most obviously, the resin had to

Table 1. Oxygen and carbon dioxide permeabilities of various polymers*

Polymer	O_2 transmission	CO_2 transmission
HDPE	2900	9100
PVC	120	500
PET	95	240
PVDC	10	75
EVOH (dry)	2	–
EVOH (humid)	100	–

*25 μm films, cm^3 per m^2 per atm pressure drop over 24h

be heavily coloured since beer rapidly goes 'off' in sunlight (*Chem. Br.*, January 2002, p 16). But a more fundamental issue was the gas permeability of the polymer. A 25 μm PET film transmits 240 cm^3 of carbon dioxide per m^2 per day per atmosphere (101 325 Pa) pressure drop across the film. This may not sound much, and is less (or much less) than the transmissions for PVC and high density polyethylene (*Table 1*), but it still means that beer in an unprotected 21 PET bottle, with a carbon dioxide pressure of 4.6×10^5 Pa would lose about a third of its fizz in six months.

Size matters

This is also true for carbonated soft drinks, but doesn't matter so much – the precise degree of carbonation is less important to the enjoyment of the product, and therefore more carbon dioxide can be put in, perhaps up to 6.1×10^5 Pa). Likewise the oxygen permeability is much more significant for alcoholic beverages than for soft drinks, and the oxygen transmission of uncoated PET is such that the beer would be undrinkable in a few months even if it hadn't lost its fizz. And as bottles get smaller their surface/volume (*S/V*) ratio increases, so such effects become even more dramatic.

Plastic food packaging therefore often requires a 'barrier layer' to prevent or reduce undesirable gas migration. One common approach is to metallise the film – aluminised polypropylene (polypropene) has a negligible oxygen transmission, and is familiar to us as the packaging material for cooked meats such as salami, and the inside of wine boxes. But metallising is relatively expensive, and would in any case destroy the aesthetics of PET. Transparent barrier polymers were therefore required. Fortunately, several were known (*Box 2*), and two have found use in beer bottling: PVDC (polyvinylidene chloride, poly-1,1-dichloroethene) and EVOH (ethylene-vinyl alcohol).

PVDC can either be co-extruded with PET while making the preform (the small bottle-shaped piece that is then blown to make the final bottle) or else the preform can be coated with the PVDC by dipping it into or spraying it with an aqueous emulsion of the resin. This was the approach used in the initial launch of the 21 beer bottle in the 1980s. Since then, however, recycling issues have come more to the fore. The alternative EVOH resin has advantages in this respect, and has captured much of the market. EVOH is co-extruded with the PET, but since it is moisture sensitive it has to be sandwiched between two layers of PET.

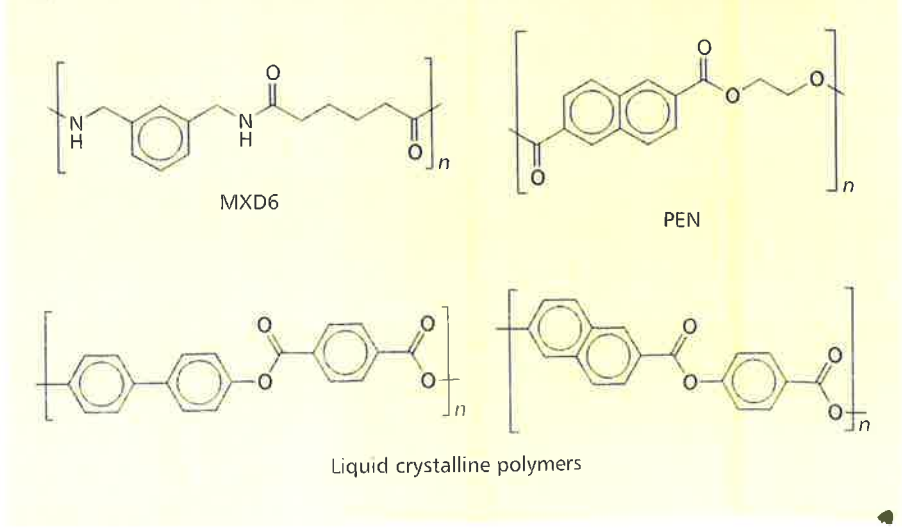
The 21 bottle rapidly secured a substantial slice of the off-licence trade in the UK, but there the market penetration stopped. We have therefore arrived at the second part of my question – why did reaching a world market with smaller bottles take so long? There are a number of reasons. Part of the answer is that brewers outside the UK didn't feel that their customers were ready for plastic beer bottles, while another part was the economics versus aesthetics equation for glass, PET and aluminium. (At the 14 fluid ounce or 0.41 pack size, aluminium cans were and are highly competitive, but were felt by the brewers to be unsuitable for premium beers. On the other hand, for the same premium beers the cost and weight of glass wasn't seen as a big problem.)

However, the main reason was chemistry – there was far more of it to be done than anybody believed. What we had in the UK in the 1980s was a PET bottle with a relatively small *S/V* ratio, which did not need to be recyclable. This contained 'flat', highly flavoured English beers with low carbonation levels, and with a distribution network that meant that filled bottles didn't need a long shelf-life. Putting fizzier, more delicately flavoured international beers into recyclable bottles with larger *S/V* ratios and distributing them across the US (where ambient temperatures can be much higher) turned out to require several technological advances.

Lot of bottle

The four problems of high carbonation levels and *S/V* ratios and long shelf-life requirements under high ambient temperatures essentially combine into one: that of reducing oxygen ingress and carbon dioxide egress through the bottle. There wasn't much that could be done at the time to improve the transmission of the PET–barrier layer combination, so attention

Fig 2. New nylons and polyesters



turned to other areas of leakage, most significantly the caps. These were originally made from nylon-6, $-(NH\text{-}(CH_2)_5\text{-}CO)_n-$, which has a gas transmission similar to uncoated PET, but latterly manufacturers have used a specialist nylon, MXD6 from Mitsubishi Gas Corporation (*Fig 2*), which owing to its high crystallinity transmits at a rate close to that of PVDC. These can also include cobalt-based oxygen scavengers and slip additives (*Box 3*).

For the issue of flavour we need to look again at *Box 1* and the most common side-product in PET manufacture: acetaldehyde (ethanal). As far as toxicity goes, this is much less of a problem than you might think. Acetaldehyde is naturally present in significant

3. Top performance

Consider your last attempt to open a supermarket bag. This simple everyday process is often tricky because of friction between the opposing polymer surfaces. Now imagine the problem multiplied a thousand-fold on a high speed packaging line. Such friction can be a serious problem during the manufacture and processing of polymer film, or in the injection moulding of plastic items.

Commercial polymer grades overcome this by incorporating special chemicals called 'slip additives'. The most effective and widely used are primary amide derivatives of naturally derived long chain fatty acids, of which erucamide (Crodamide ER) and oleamide (Crodamide OR) are the most common types. These additives, incorporated at low concentrations, migrate through the polymer to form microscopic invisible slippy layers at the polymer surface, so providing the slip or mould release effect.

An interesting feature of fatty amides is that slip performance is closely linked to chemical structure. For example, the *cis* double bond at the centre of the fatty chain in erucamide and oleamide appears vital for slip performance. If the double bond is altered to the *trans* orientation, moved to a different position in the fatty chain, or is removed completely to give the saturated analogues behenamide and stearamide then the slip performance is dramatically reduced.

It is believed the link between structure and performance lies in the way amide molecules pack at the polymer surface. Molecular modelling studies suggest that linear molecules like behenamide pack tightly together to form a rigid crystalline surface structure that resists lateral movement. By contrast molecules with a *cis* double bond have a less densely packed surface structure, which allows lateral deformation and hence slip between the layers of amide and the polymer surface.

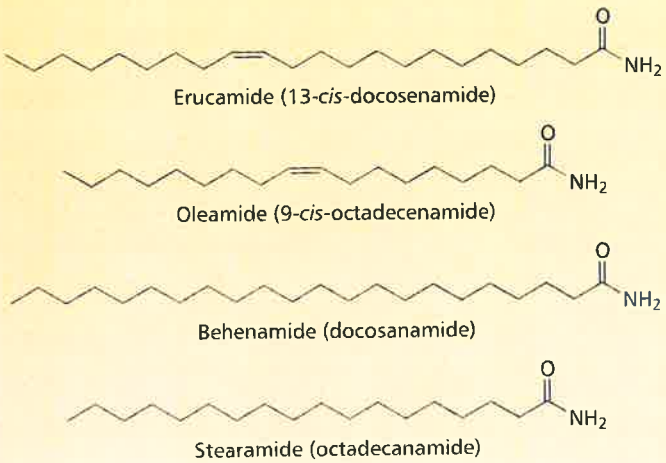
In plastic bottle caps the slip additives have two roles to fulfil. Migrating to the surface of the cap, they give good release during injection moulding, but more importantly they give the slip or torque release effect which allows the cap to be twisted easily on and off the bottle.

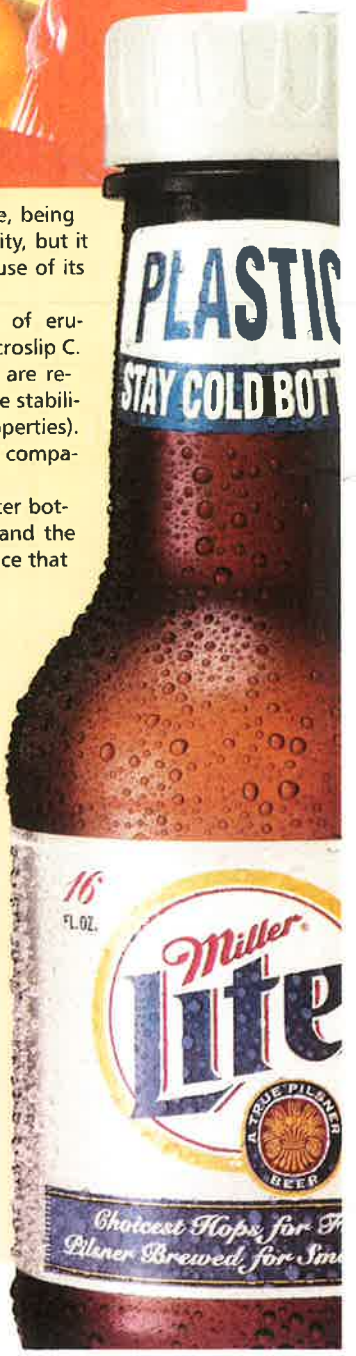
Special factors apply when designing slip additives for bottle caps. Organoleptic (taste and odour) properties are equally as important as torque release, especially in the rapidly growing area of bottled water. Because erucamide is made from a natural raw material it can contain low levels of compounds that are oxidatively unstable. Any breakdown products can potentially contribute to taste and odour. Behenamide, being a saturated molecule, has very good stability, but it is not suitable for many applications because of its poor slip performance.

Croda has developed a special grade of erucamide specifically for bottle caps called Incroslip C. With Incroslip C the problem compounds are removed, resulting in extremely high oxidative stability (and hence improved organoleptic properties). This new material is now being tested by companies around the world.

So next time you twist the cap off a water bottle, spare a thought for the slip additive and the science involved in ensuring you never notice that it is there.

David Cherry, sales & marketing manager, Croda. For more information contact Croda at sales@croda-universal.com



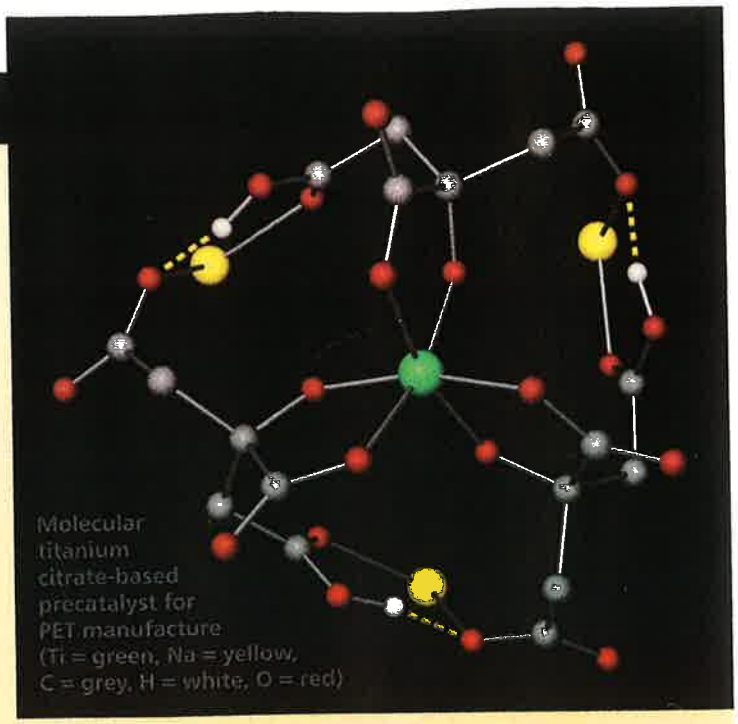


4. Fast work

Around 25m t of PET fibre, resin and film was produced in 2001, with the associated PET catalyst market having a value of around £55m pa. Traditionally, polyester manufacturers have looked to developments in polymer processing to generate new products and markets for PET. For example, two of the major PET growth areas are high modulus low shrinkage (HMLS) yarn and improved bottle technology.

Polycondensation, on which polyester manufacture predominantly relies, is intrinsically less controllable than the chain-growth mechanism by which olefin polymerisation occurs. However, a number of recent developments herald a more sophisticated and molecular approach to catalyst design in the polyester industry and the stage is now set for 'designer' catalysts to drive new polyester applications.

This 'molecular' philosophy has already found its way into industrial PET manufacture. Catalyst company Synetix has recently commercialised a molecular titanium citrate based PET catalyst precursor as a replacement for current antimony oxide technology. The problem was titanium complexes are inherently unstable in the presence of water due to their 'oxophilicity' or tendency to attract oxygen. A key target for researchers, at Synetix and the University of Bath, was to improve the hydrolytic stability of the catalyst. Our answer lay in using citrate ligands to stabilise the resulting Ti catalyst (*Fig 1*). The resulting catalyst not only increased reaction throughput (by reducing catalyst deactivation), but has also led to reduced haze in the finished PET article. Both of these features are highly desirable in the industry.



Molecular titanium citrate-based precatalyst for PET manufacture (Ti = green, Na = yellow, C = grey, H = white, O = red)

Isolation and X-ray crystallography reveals that the pre-catalyst comprises a single Ti centre with a C_3-symmetric arrangement of citrate ligands surrounding the metal.[1] This highly active complex may be used at much lower concentrations than conventional antimony catalysts, which reduces the metal content of the final polyester by more than 90 per cent. The reduced metal content has many benefits, including brighter polymer for bottles and fewer breakages in fibres. Furthermore, the molecular arrangement of the three citrate ligands allows the possible introduction of other catalytic metal centres. Such developments will provide a new family of multifunctional catalysts in the future.

Another key development in polyester chemistry is taking place at the high-value end of the polymer market. There is much current interest in polyesters such as polylactic acid (PLA) that are biocompatible, biodegradable and derived from renewable sources (*Chem. Br.*, April 2002, p 40). The method of choice for polymerisation in these cases is not polycondensation, but living ring opening polymerisation from cyclic starting materials such as dilactide and ε-caprolactone. The design of single-site molecular catalysts based on detailed mechanistic insight is yielding impressive results, facilitating control over polymer molar mass, polydispersity and end-group functionality of the resulting polymers.

On another front, progress has recently been made in rendering polycondensation itself a controlled, living process by the judicious choice of monomer and well-defined molecular initiators. In the example in the *Scheme below*,[2] controlled polycondensation is achieved by using a low concentration of a crown ether to solublise a solid potassium benzoate initiator before reaction with a growing polymer chain in the liquid phase. These phase transfer conditions transform what is essentially a polycondensation reaction into a controlled chain-growth process, thereby making the process easier to control.

These developments and others suggest that the polyester industry is at last turning towards the molecular design of catalysts and initiators. Future advances in this area will surely lead to cleaner, more efficient processes able to produce polymers with well defined physical properties and chemical functionalities. □

Matthew Davidson is professor of chemistry at the University of Bath, e-mail: m.g.davidson@bath.ac.uk; and Martin Partridge is technology manager, polyester catalysts, at Synetix in Billingham, Cleveland.

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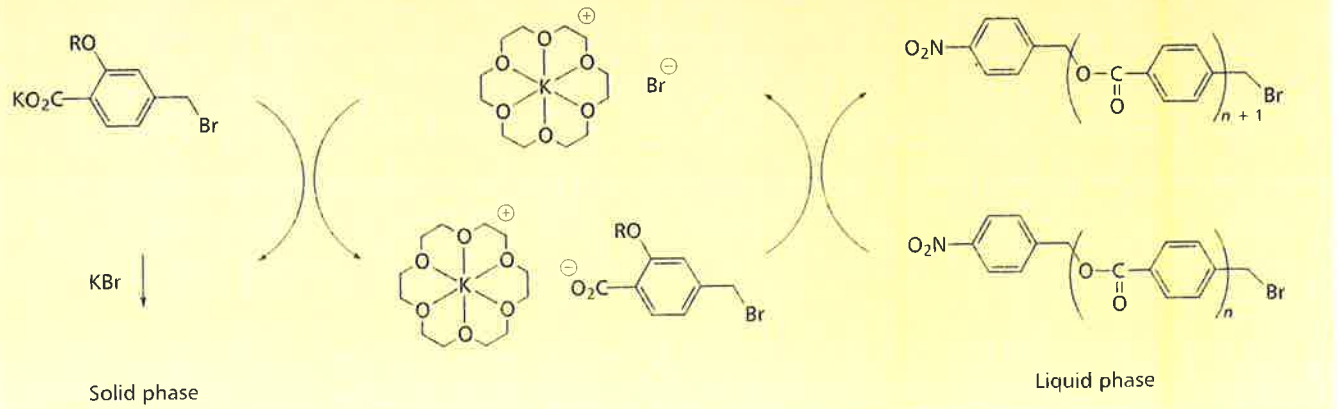

quantities (up to 230 ppm) in many ripe fruits and dairy products. It is even listed as a food additive for enhancing citrus flavours. The levels found in PET are in the region of 5–10 ppm, but even at such low levels this can be detectable in bottled mineral waters and in principle lightly flavoured beers. The industry therefore adjusts the manufacturing process for food grade PET to bring this level down as far as possible.

Another look at *Box 1* will suggest another possible problem with PET as a food packaging material: the antimony trioxide catalyst. Once again this is less of a worry than one might imagine, for two reasons. First, the catalyst is only present at low levels in the resin and is relatively immobile in the solid polymer matrix. Secondly, the oxide is one of the least toxic antimony compounds. Animal feeding studies have shown that a diet containing 20 g kg^{-1} body weight (many orders of magni-

tude higher than could be obtained from leaching out of bottles) gave no adverse effects. Nevertheless, there have been studies into alternative catalyst materials, and these are now showing considerable promise in terms of improved manufacturing efficiency (*Box 4*).

And finally, there is the vexed issue of recycling. The green ideal would be for the bottles to be reused, but washing and sterilising would be uneconomic, and has its own negative environmental impact. PET resin itself is readily recyclable, and recycling is also possible with barrier layers, but the recycled material couldn't be risked in contact with food or drink, and is largely used for non-food applications. However, one promising approach is to use it as the 'outside' layer of a PET–EVOH–PET sandwich, with fresh food grade resin on the inside.

A rosy future?

Having finally made the breakthrough and appeared in smaller bottles in the international market, is the future therefore rosy for PET in beer bottles? Probably, but perhaps not. Certainly the PET–PVDC and PET–EVOH–PET combinations appear to be under threat from alternative barrier materials. These can be either organic, such as the Bairocade epoxy-based coating promoted by PPG Industries in the US, or inorganic, such as the plasma-deposited amorphous carbon layer proposed by the French company Sidel. But there are also icebergs on the horizon for the PET resin itself. Newer speciality nylons and polyesters have excellent barrier properties, which mean that the barrier layer could be disposed of entirely. Currently these would be too expensive for beer bottles, but as they find other applications their costs are coming down.

We have already seen MXD6 appearing as a cap material. Other examples include the liquid crystalline polyesters (LCPs), Vectra (from Celanese) and Xydar (from BP Amoco). LCPs contain linear aromatic polyester groups, some examples of which are shown in *Fig 2*. The polymer molecules are therefore essentially rigid rods which crystallise in highly ordered arrays on cooling from the melt, giving gas barrier properties superior even to EVOH. (In fact, the rigid groups need to be separated by more flexible segments in the commercial polymers, but the barrier properties are nevertheless very impressive.) A related candidate, also shown in *Fig 2* is PEN. This is not sufficiently rigid to give liquid crystalline melts, but is cheaper than LCPs while having an oxygen permeability intermediate between PET and PVDC.

The techno-economic and environmental contests between glass, aluminium and plastic for beer bottles are both now finely balanced. The next few years should see a clear favourite emerging. And my money would be on plastics.

Dave Birkett is a senior scientist working for Loctite RD&E, Dublin, Ireland.

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